

Spin dynamics of S-state ions in the filled skutterudites $\text{La}_{1-x}\text{R}_x\text{Pt}_4\text{Ge}_{12}$ ($R = \text{Gd}, \text{Eu}$)

F.A. Garcia, R. Gumeniuk, W. Schnelle, J. Sichelschmidt, A. Leithe-Jasper, Yu. Grin, F. Steglich
Max-Planck-Institut für Chemische Physik fester Stoffe, Nothnitzer Strabe 40, 01187 Dresden, Germany.

(Dated: 02/09/12)

A detailed study of the spin dynamics of the S-state ions Gd^{3+} and Eu^{2+} in the filled skutterudites $\text{La}_{1-x}\text{R}_x\text{Pt}_4\text{Ge}_{12}$ ($R = \text{Gd}, \text{Eu}$) is reported. The spin dynamics is investigated directly by means of Gd^{3+} and Eu^{2+} electron spin resonance (ESR), performed at X-band (≈ 9.4 GHz) and Q-band (≈ 34 GHz) frequencies in the temperature intervals $8 < T < 300$ K and $1.5 < T < 300$ K respectively. The ESR parameters provide direct evidence for the vibrational behavior of the Gd^{3+} ions but not for the Eu^{2+} ions. These results are interpreted in the light of recent discussions about the spin relaxation in cage systems. In particular, the Gd^{3+} spin relaxation in $\text{La}_{0.9}\text{Gd}_{0.1}\text{Pt}_4\text{Ge}_{12}$ provide evidence for the existence of an extra phonon mode with an Einstein temperature $\theta_E \approx 24$ K in this system. The work suggests that the so-called “rattling” modes have a general and important role that should be taken into account in the study of spin dynamics in cage systems.

I. INTRODUCTION

Several families of intermetallic compounds are today known to crystallize in cage-like structures. A topic of growing interest in this broad area of research is the role of the lattice dynamics in the physical properties found in these materials. Among these cage systems, the family of the filled skutterudites has been attracting special attention triggered by the wide range of physical phenomena found in these compounds. These include exotic strongly correlated ground states [1] as well as a relatively large Seebeck coefficient, which opens the perspective of using skutterudites in the construction of thermoelectric devices [2].

Filled skutterudites have the general formula $\text{R}_y\text{T}_4\text{X}_{12}$ and crystallize in the $\text{LaFe}_4\text{P}_{12}$ structure with space group $Im\bar{3}$ and local point symmetry T_h for the R ions [3]. The R element is usually referred as *guest*, or *filler*, and resides in the large void in the framework of the $[\text{T}_4\text{X}_{12}]$ *host* structure. Systematic analysis of the chemical bonding in skutterudite compounds [4, 5] revealed a fundamental role of the R ions in the stabilization of the crystal structure.

It is generally accepted that in many of these compounds, a substantial change in the collective vibrational dynamics of the system is implied by the dynamical behavior of the R ions [6, 7]. In the simplest approximation, the R-ion dynamics is described in terms of a localized and isolated phonon mode, usually called “rattling” mode, and it can be fully described by a single parameter θ_E , the Einstein temperature [8–10]. However, the nature and role of the total vibrational dynamics has been a matter of intense debate in the field, and there are a growing number of experimental [6, 7, 11–14] and theoretical [15–17] investigations demonstrating the inadequacy, and exploring possible extensions, of this scenario. Of special interest for the present work are current studies of the spin dynamics in skutterudites, and also in other cage systems, by means of electron spin resonance (ESR) and also nuclear magnetic resonance (NMR) [18–25].

A recent theoretical work by Dahm *et al.* [26] investigated the NMR relaxation from rattling modes, includ-

ing anharmonic ones. It was found that, even in metallic skutterudites, the rattling behavior may give rise to an important contribution to the spin relaxation by means of a Raman process (two-phonon coupling) which would coexist with the usual Korringa process (conduction-electron scattering). Recent NMR experiments in the skutterudites $\text{LaOs}_4\text{Sb}_{12}$ [19] and $\text{LaPt}_4\text{Ge}_{12}$ [23] have successfully identified an additional contribution to the Korringa relaxation, that was analyzed in the framework of the above cited theory [26]. The relaxation at the La site was shown to be field independent, which was interpreted as a piece of evidence for a non-magnetic origin of this additional relaxation.

In a recent work, the spin dynamics of Eu^{2+} in the $\text{EuT}_4\text{Sb}_{12}$ ($T = \text{Fe}, \text{Ru}, \text{Os}$) skutterudites was investigated by ESR [22] and clear signatures of the Eu^{2+} dynamical behavior were observed. It was found that the ESR linewidth ΔH , as a function of temperature, peaks at about θ_E and increases linearly at higher temperatures. Nevertheless, in contrast with the NMR experiments, the ESR results were shown to be field dependent. Thus, the results were ascribed to inhomogeneities of the spin-spin interaction, implied by the rattling modes. It was suggested that these inhomogeneities are quenched at high fields, causing the above features in ΔH to disappear.

A fundamental issue in the application of ESR to probe the interplay of localized spins and the guest-ion dynamics in metallic skutterudites is the bottleneck effect [27]. The bottleneck effect in metals occurs when the conduction electron (ce)-lattice (L) relaxation time ($1/T_{\text{ceL}}$) is slow in comparison with the conduction electron-localized spin (S) relaxation time ($1/T_{\text{ceS}}$). Hence, after receiving energy from the localized spins, the conduction electrons instead of dissipating energy to the lattice, give this energy back to the localized spins. As a consequence, the relaxation of the localized spins is now modulated by the slow $1/T_{\text{ceL}}$. In turn, one should always be careful in drawing any conclusions about a relation between effects in ΔH and effects in the exchange interaction between the local and itinerant spins.

Aiming to discuss the applicability of the ESR tech-

nique in the study of the spin dynamics in cage systems, here, we present at two microwave frequencies (X - and Q -band) the ESR spectra of Gd^{3+} and Eu^{2+} (configuration $J = S = 7/2$, $L = 0$) in $\text{La}_{1-x}\text{R}_x\text{Pt}_4\text{Ge}_{12}$ ($R = \text{Gd}$, Eu) for various values of x . Choosing S-state ions, we rule out non-trivial crystal-field (CF) effects implied by the local T_h symmetry of the “filler” site [28]. In addition, we address the difference between the substitution of La^{3+} by small amounts of Gd^{3+} (isoelectronic substitution) and Eu^{2+} (hole doping).

The filled skutterudite $\text{LaPt}_4\text{Ge}_{12}$ is a metallic compound which undergoes a superconducting transition at $T_{\text{sc}} = 8.3$ K [29]. Electronic structure calculations show that the Fermi surface of this compound is mainly composed by $4p$ orbitals from the Ge atoms, with rather small contributions derived from the Pt $5d$ orbitals. Magnetization measurements show no signs for magnetic fluctuations or itinerant moments. The superconducting state, however, is not yet fully understood [30, 31] and we address the partial suppression of the superconducting state due to the inclusion of Gd^{3+} moments.

The paper is organized as follows: first, we present and discuss our experiments with the Gd doped samples. Then, we contrast these results with the experiments on the Eu-doped sample and also with $\text{EuPt}_4\text{Ge}_{12}$. Afterward, we explore our results in the context of relaxation from rattling modes [26].

II. EXPERIMENT

Single-phase polycrystalline samples of $\text{La}_{1-x}\text{Gd}_x\text{Pt}_4\text{Ge}_{12}$ ($x = 0.005, 0.01, 0.05$ and 0.1) and $\text{La}_{1-x}\text{Eu}_x\text{Pt}_4\text{Ge}_{12}$ ($x = 0.01, 0.05, 1$) were prepared as described elsewhere [5, 29]. To verify the content of the S-state ions, the temperature dependence of the DC susceptibility of each sample was measured and the experimental results were fitted to a Curie-Weiss behavior, assuming the full effective moment $\mu_{\text{eff}} = 7.93 \mu_B$ for both Gd^{3+} and Eu^{2+} ions. These measurements were performed in a commercial SQUID magnetometer (Quantum Design). The ESR measurements were performed in a Bruker Elexsys 500 spectrometer at both X -band ($\nu = 9.4$ GHz) and Q -band ($\nu = 34.4$ GHz) frequencies, in the temperatures intervals $8 < T < 300$ K and $1.5 < T < 300$ K respectively. The Q -band measurements at relatively lower temperatures were possible because the typical applied magnetic fields close to the resonance field H_{res} at Q -band ($H_{\text{res}} \approx 1.2$ T, see below) used in the ESR measurements are larger than the upper critical field H_{c2} ($H_{c2} \approx 1$ T at $T \approx 7$ K) measured for $\text{LaPt}_4\text{Ge}_{12}$ [5].

The samples were powdered and sieved (gritting of $40\mu\text{m}$) for grain size homogeneity. The size of these grains is still much larger than the skin depth that can be estimated from the resistivity measurements in the temperature interval of the experiment. Hence, we observed an asymmetric resonance line that was fitted as

described in Ref. [32]. The parameters included in the fitting are the ESR linewidth ΔH , the resonance field H_{res} , which defines the ESR g -values by applying the resonance condition $\hbar\nu = g\mu_B H_{\text{res}}$, the resonance amplitude and an $\alpha = D/A$ parameter expressing the ratio between the dispersion (D) and absorption (A) of the microwave radiation when it probes a metallic material.

III. RESULTS AND DISCUSSION

A. ESR on $\text{La}_{1-x}\text{Gd}_x\text{Pt}_4\text{Ge}_{12}$

An ESR experiment probing a small amount of paramagnetic ions in a non-paramagnetic host lattice is supposed to bring important information concerning not only the ionic impurity state but also the host. In the present case, Gd is an isoelectronic substitution and is expected to have only a local effect on the lattice parameter.

In Fig. 1 we show some selected ESR spectra taken at both X -band and Q -band frequencies. In the whole temperature interval, we observe a single Lorentzian line-shape and, even in the lowest temperature of the experiment, no sign of unresolved CF effects were observed in the powder spectra.

Fig. 2 shows the low-temperature X -band ESR linewidth (ΔH) for four different substitutions of Gd. It is clear that there are no concentration effects in the order of magnitude of ΔH . In the figure, the continuous line is the fitting to the usual Korringa expression $a + bT$. The residual linewidth a is larger for lower concentrations. This quantity is expected to be determined by CF effects, dipolar interactions and spin-spin exchange narrowing. The latter effect renders the residual linewidth narrower for higher concentrations and seems to be dominating over the broadening effects of the dipolar fields. The important result, however, is that the apparent Korringa rate b is concentration independent.

In the context of the bottleneck effect, we recall that since $1/T_{\text{ceS}}$ is directly proportional to the concentration of the ESR probe (Gd^{3+} ions in this case), an increase of this concentration should slow down even more the apparent relaxation rate. Thus, the hallmark of a bottlenecked system is a concentration-dependent relaxation. The ESR ΔH should evolve as in a Korringa-like relaxation $\Delta H(T) = a + \frac{\beta}{x}T$, where β is a constant, which in first approximation does not depend on the exchange interaction, x is the concentration of the ESR probe and a is the residual linewidth $\Delta H(T = 0)$. The physics of the bottleneck effect was well explored in the classical ESR literature [33–35] and also in the review by Barnes [27].

Our result indicates that the system is non-bottlenecked even for relatively high concentrations. From our previous discussion, one can realize that there are two possible routes for opening a bottleneck, being either increasing $1/T_{\text{ceL}}$ or lowering $1/T_{\text{ceS}}$. In $\text{LaPt}_4\text{Ge}_{12}$, the conduction electrons at the Fermi surface originate

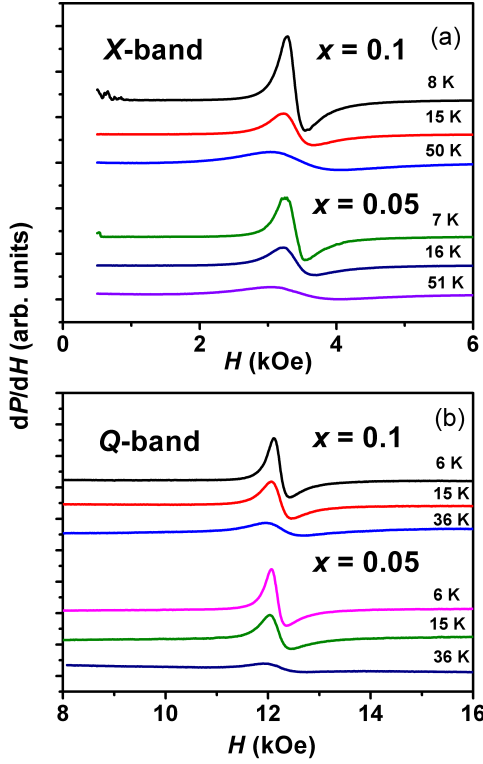


Figure 1: (Color online) Selected a) X-band and b) Q-band ESR spectra of the derivative of the resonance absorption (dP/dH) for $\text{La}_{1-x}\text{Gd}_x\text{Pt}_4\text{Ge}_{12}$ ($x = 0.1$ and $x = 0.05$). A single asymmetric Lorentzian lineshape is observed in the whole temperature interval covered by the experiment.

mainly from the Ge $4p$ electrons, which are more strongly coupled to the lattice than s -band electrons would be. This contributes to the increase of $1/T_{\text{ceL}}$. On top of this effect, one should also consider that the modification of the total vibrational dynamics of the system, as implied by the partial substitution of La by Gd, contributes to the scattering of the conduction electrons thus also increasing $1/T_{\text{ceL}}$.

In the non-bottlenecked regime the spin relaxation of a paramagnetic ion in a metallic host should be described by the Korringa process. The expected value for the Korringa rate (for a q -independent exchange coupling and in the absence of multi-band effects) is given by [27]:

$$b = \frac{\pi k_B}{g\mu_B} \Delta g^2 \quad (1)$$

where Δg is the so-called g -shift, which occurs in metals due to the exchange interaction between the localized spins and the conduction electrons [27]. A g -shift is calculated in reference to the g -values of experiments in insulators ($\Delta g = g_{\text{exp}} - g_{\text{ins}}$). Adopting the low- T value of the g -shift, we have $\Delta g = 0.009(4)$. The obtained value for the Korringa rate ($b \approx 2.3$ Oe/K) is much lower than the one observed. Going through the relation between b , Δg and the exchange interaction in more detail, we write

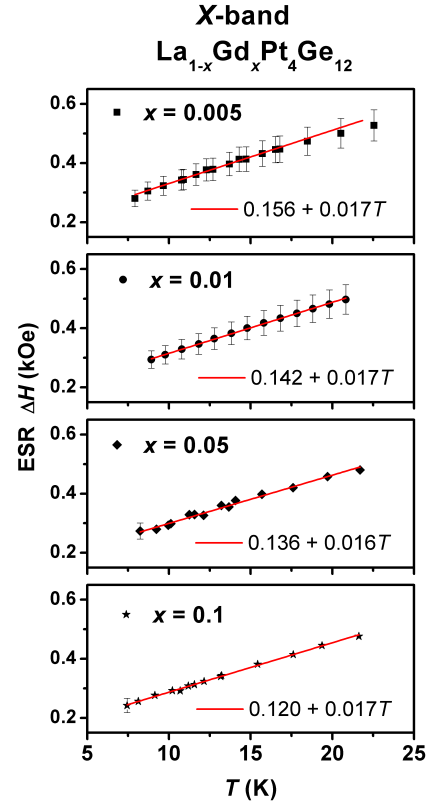


Figure 2: (Color online) Low-temperature X-Band ESR linewidth (ΔH) for different substitutions of Gd in $\text{La}_{1-x}\text{Gd}_x\text{Pt}_4\text{Ge}_{12}$. The thick line is the linear fitting to the expression $\Delta H(T) = a + bT$ and the obtained parameters are shown in the figures.

the full expression for both quantities [27]:

$$\begin{aligned} \Delta g &= \langle \eta(E_F) J(q=0) \rangle_{\text{Av}} = \eta(E_F) \langle J(q=0) \rangle_{\text{Av}} \\ &\equiv \eta(E_F) J_1 \end{aligned} \quad (2)$$

$$\begin{aligned} b &= \frac{\pi k_B}{g\mu_B} \left(\langle (N(E_F) J(k_F, k'_F))^2 \rangle_{\text{Av}} \right) = \frac{\pi k_B}{g\mu_B} \eta(E_F)^2 \langle J(q)^2 \rangle_{\text{Av}} \\ &\equiv \frac{\pi k_B}{g\mu_B} \eta(E_F)^2 J_2^2 \end{aligned} \quad (3)$$

where in equations 2 and 3 the brackets denote an average over the Fermi surface and $\eta(E_F)$ is the density of states for a given spin direction at the Fermi surface (states $\text{eV}^{-1}\text{mol}^{-1}\text{spin}^{-1}$). From these, one can see that Δg is a homogeneous polarization of the Gd^{3+} spins due to the exchange interaction with the conduction electrons, whereas b is related to a scattering process. Thus, in writing Eq. 1 we have assumed $J_1 = J_2$ which does not seem to be the case in our experiment.

As extensively discussed in the literature [27, 33, 35], this contrast, in the absence of a bottleneck, may have its origin in multi-band and/or electron-enhancement effects. However, previous works on the host compound do not support either the presence of different electronic contributions to the Fermi surface or significant electronic correlations [29]. We shall also discuss this issue later in this section, in connection with our Q -band measurements.

A general analysis of the bottleneck phenomenon [27] shows that, if the spin-orbit scattering due to the magnetic impurity (meaning the dependency of $1/T_{\text{ceL}}$ on the amount of Gd^{3+} spins) is stronger than the effective exchange scattering (that favors the Korringa relaxation), the system is non-bottlenecked. Pursuing this line, we suggest that, even if the homogeneous polarization (given by Eq. 2) is small, the exchange scattering process could be enhanced by the rattling modes. In this interpretation, the rattling modes are involved in the exchange scattering process which still dominates the relaxation.

The suppression of the superconducting state ($\Delta T_{\text{sc}} = T_{\text{sc}}(x=0) - T(x)$) by a given concentration (Δx) of magnetic impurities is also given by an effective exchange scattering usually comparable with the exchange scattering given by the ESR [35]. The process is described by the Gorkov-Abrikosov expression:

$$\left| \frac{\Delta T_{\text{sc}}}{\Delta x} \right| = \frac{\pi^2}{8k_B} J_{\text{eff}}^2 \eta(E_F) (g_J - 1)^2 J(J+1) \quad (4)$$

where J_{eff} is the effective exchange scattering, g_J is the Landé gyromagnetic factor, and J is the impurity total angular momentum (here $J = S$, since for Gd^{3+} $L = 0$). In Fig. 3 we show the rather small suppression of T_{SC} by the effect of magnetic impurities. The data was obtained from magnetization measurements measured in warming in 20 Oe field after zero field cooling. T_{SC} was defined by extrapolation of the steepest slope of $\chi(T)$ to $\chi(T) = 0$. Using the calculated density of states at the Fermi level [29] $\eta(E_F) = 13.4 \text{ states eV}^{-1} \text{f.u.}^{-1} = 15.8 \text{ states eV}^{-1} \text{mol}^{-1} \text{spin}^{-1}$ in Eqs. 3 and 4, we obtain the following estimate for the effective exchange scattering: $J_{\text{eff}}^{\text{ESR}} = 1.54 \pm (0.40) \text{ meV}$ and $J_{\text{eff}}^{\text{sc}} = 1.24 \pm (0.20) \text{ meV}$, which agrees reasonably well with $J_{\text{eff}}^{\text{ESR}}$ and make a strong case in favor of a relaxation process governed by the exchange interaction. It is also a piece of evidence that the relaxation is not in a bottleneck regime. Nevertheless, we still lack a mechanism for the enhancement of $J_2 = J_{\text{eff}}$ in comparison with J_1 from Eq. 2.

Figure 4(a) shows the X -band ΔH for the two highest concentrations ($x = 0.05$ and $x = 0.1$) which allows one to follow the temperature evolution of the resonance spectra up to higher temperatures, still with relatively high resolution. It is shown that ΔH deviates from the apparent linear behavior at low T . Furthermore, the data suggest that the high temperature relaxation regime has a weak dependence on the concentration of the ESR probe. In previous ESR experiments in metal-

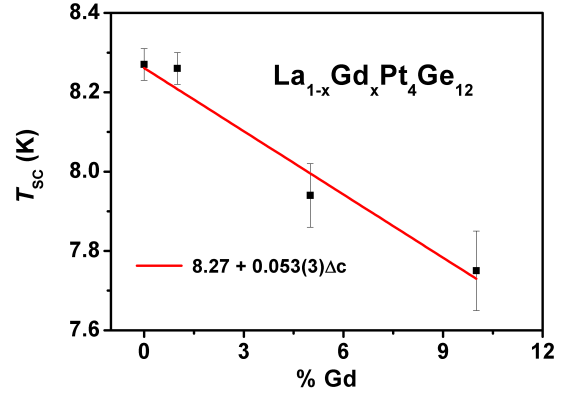


Figure 3: (Color online) Suppression of the superconducting state in $\text{La}_{1-x}\text{Gd}_x\text{Pt}_4\text{Ge}_{12}$ by the inclusion of Gd impurities. The thick line is the linear fit to our experimental data. The value of $T = 8.27 \text{ K}$ is the transition temperature (T_{SC}) for the pure $\text{LaPt}_4\text{Ge}_{12}$ compound.

lic cage systems, $d(\Delta H)/dT$ was also shown to be non-constant [18, 20]. In particular, it was found that the deviations from the linear behavior may appear as a “kink” in $\Delta H(T)$, which defines a low-temperature and a high-temperature Korringa-like rate [20].

In the above cited works [18, 20], it was speculated that the origin of the temperature dependence of $d(\Delta H)/dT$ is due to some reorganization of the Fermi surface implied by structural effects and its concomitant changes in the band structure [18, 20]. In addition, it is generally accepted that by multiple filling (filled skutterudites with more than one element as guest) one can induce a larger disorder in the lattice structure of the material, thus causing a broadening in their phonon spectra [36, 37]. In this sense, the origin of the concentration dependence of $d(\Delta H)/dT$ at high temperature can be explained by a combination of both effects: a change in the disorder of the phonon spectra, due to different Gd concentration, would lead to a different energy scale where the putative reorganization of the Fermi surface takes place resulting in a weak dependence of the high temperature relaxation on the Gd concentration. However, we would like to point out that, as implied by Eqs. 2 and 3, similar effects would rise due to changes in the exchange scattering.

Any effect in the Fermi surface, as well in the exchange scattering, would also be reflected in the ESR g -values. Therefore, the observed change of about 1/2 in the value of b should also manifest itself in the g -values. In Fig. 4(c) we present these data, again for the $x = 0.05$ and $x = 0.1$ samples. Although the result is encouraging, one should take it carefully, since the estimated error bars are about half the total variation. However, our data clearly suggests a downturn in the g -values.

The vibrational dynamics of the guest ion may give rise to local inhomogeneities of the crystal field which could in principle appear in an ESR experiment as an inhomogeneous broadening of the resonance [38]. This may be

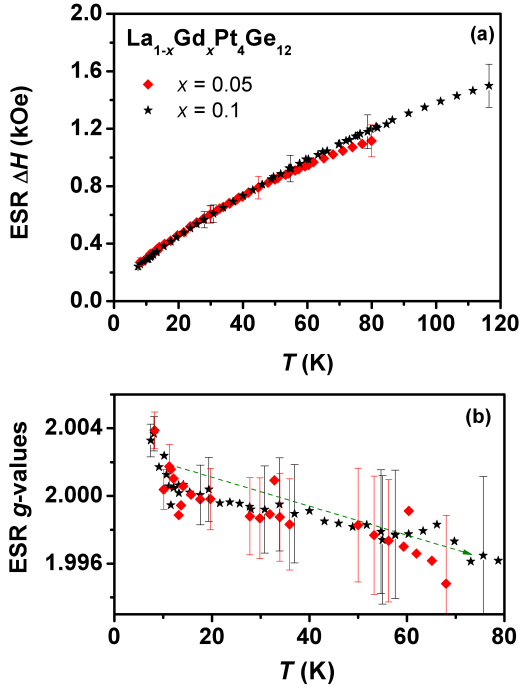


Figure 4: (Color online) (a) X band ESR linewidth (ΔH) ($8 \leq T \leq 120$ K) and (b) X-band ESR g -values for $\text{La}_{1-x}\text{Gd}_x\text{Pt}_4\text{Ge}_{12}$ with $x = 0.05$ and $x = 0.1$. The dashed line is a guide to the eye (see text for a discussion).

revealed in an experiment at higher frequencies. In Fig. 5(a)-(b) we show our Q -band measurements. It is noteworthy that no such broadening takes place, demonstrating that the resonances are homogeneous. This means that no static disorder is being detected in our experiment (compare the order of magnitude of ΔH in these figures and Fig. 4 (a)-(b)).

In Fig 5(a) one can note that ΔH broadens at low temperature, probably due to spin-spin interactions. Figure 5(a) also shows that above the temperature at which the low-temperature magnetic fluctuations cease to dominate ΔH ($T \gtrsim 10$ K), the evolution of ΔH with temperature is fairly described by a linear behavior with $b = 12$ Oe/K. To highlight this difference, we present in Fig. 5(b) the X -band and Q -band ΔH for the sample $\text{La}_{0.95}\text{Gd}_{0.05}\text{Pt}_4\text{Ge}_{12}$. In the Q -band measurements, a systematic variation of the g -values was not observed and a concentration and temperature independent g -value of $g = 2.011(5)$ was found. The expected Korringa rate (Eq. 1) obtained from this result is $b = 9$ Oe/K which in turn indicates, within experimental error, that in the experiment at Q -band the relaxation of the Gd^{3+} ions follows the simple picture given by Eq. 1. Therefore, our disregard of multiband effects in the analysis of the X -band data is also supported by these results, since one cannot expect that the typical fields involved in the Q -band measurements would eventually suppress any multiband effects.

Put together, these results favors the idea that, as far

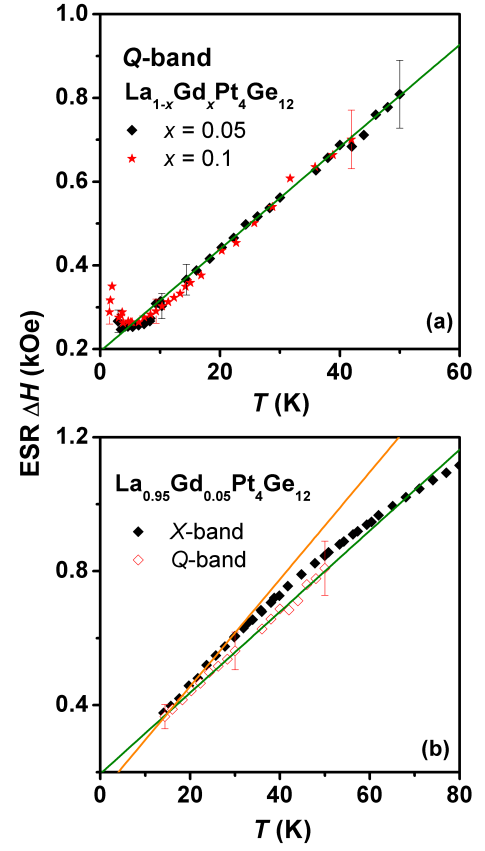


Figure 5: (Color online) a) Q -band ESR linewidth (ΔH) for $\text{La}_{1-x}\text{Gd}_x\text{Pt}_4\text{Ge}_{12}$ ($x = 0.05$ and $x = 0.1$). The thick line is the linear fit to the expression $\Delta H(T) = a + bT$ and the obtained parameters are $a = 195(1)$ Oe and $b = 12(1)$ Oe/K. Again, no concentration dependency of ΔH (apart from the low-temperature broadening) is observed. (b) Q -band and X -band data for $\text{La}_{0.95}\text{Gd}_{0.05}\text{Pt}_4\text{Ge}_{12}$.

as ESR is concerned, the rattling behavior manifests itself through a coupling with the exchange interaction. A more comprehensive discussion on this topic will be given by the end of section C. Now, we point out that it has been recognized [39] that the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction may give rise to inhomogeneous broadening and shift of the ESR spectra. Hence, it is plausible that an intricate relation between the Gd^{3+} rattling and the RKKY interaction between the Gd^{3+} spins, explains our results.

We mention again that such field dependence of the relaxation was not reported in the NMR experiments [19, 23]. We also stress that the absence of static inhomogeneities is an important sign of the sample quality, in particular, it demonstrates that the Gd ions are homogeneously distributed in the sample.

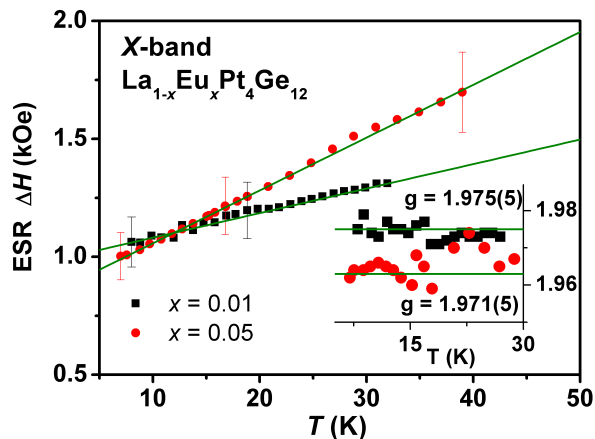


Figure 6: (Color online) X-band ESR linewidth (ΔH) for $\text{La}_{1-x}\text{Eu}_x\text{Pt}_4\text{Ge}_{12}$ ($x = 0.01$ and $x = 0.05$). The thick line is the linear fit to the expression $\Delta H(T) = a + bT$. For $x = 0.01$ the obtained coefficients are $a = 977$ Oe and $b = 10.5(5)$ Oe/K whereas in the case $x = 0.05$ the coefficients are $a = 834(5)$ Oe and $b = 22.5(3)$ Oe/K. The inset shows a temperature independent g -value of about $g = 1.975(5)$, for $x = 0.01$, and $g = 1.963(5)$ for $x = 0.05$, implying in a negative g -shift (see text for discussion).

B. ESR on $\text{La}_{1-x}\text{Eu}_x\text{Pt}_4\text{Ge}_{12}$ and $\text{EuPt}_4\text{Ge}_{12}$

The partial substitution of La for Eu adds one hole to the Fermi level per f.u.. Thus, it is expected that this local electronic inhomogeneity gives rise to interesting effects in the interaction of the Eu^{2+} spin with the conduction electrons.

We present in Fig. 6 the X-band ESR ΔH for $\text{La}_{1-x}\text{Eu}_x\text{Pt}_4\text{Ge}_{12}$ ($x = 0.01$ and $x = 0.05$). Again, no signs of a bottleneck effect were found. In comparison with our previous discussion, the huge residual linewidth ($a \approx 1000$ Oe) is most likely due to relatively larger CF effects [27]. In the inset of Fig. 6, the thick solid lines represent the average of the measured g -values for each sample. From these values, one obtains relatively large $\Delta g = -0.018(5)$ and $\Delta g = -0.030(5)$ for the $x = 0.01$ and $x = 0.05$ samples, respectively. These g -shifts (c.f. Eq. 1) give a Korringa rate of $b = 9(3)$ Oe/K and $b = 28(8)$ Oe/K, respectively. In the former case, the measured Korringa rate is $b = 10.4(5)$ Oe/K and in the latter case $b = 22.4(5)$ Oe/K. Therefore, a comparison of the results suggests that for both $x = 0.01$ and $x = 0.05$, the Eu^{2+} relaxation fits in the simple picture of Eq. 1.

A negative Δg originates from a covalent mixing between localized and itinerant states [27, 40]. In the case of $4f$ impurities, a negative Δg results from the mixing of $4f$ states and d itinerant electrons. Thus, our results, for both the Korringa rates and g -shifts, ask for a significant change of the local electron density at the Eu impurities, even for small substitution of La by Eu.

Different from the Gd case, the ternary $\text{EuPt}_4\text{Ge}_{12}$ compound was available for studies. Figure 7 presents

our results. Here we find $\Delta g = -0.035(5)$ (for $T \gtrsim 20$ K), implying, by Eq. 1, a Korringa rate $b \approx 34$ Oe/K. The measured Korringa rate for the concentrated $\text{EuPt}_4\text{Ge}_{12}$ system is $b = 8.7(3)$ Oe/K. This enormous contrast is usually attributed to the q -dependency of the exchange coupling J_{eff} , and provides evidence for an indirect exchange interaction between the localized spins of the RKKY type [41].

Alternatively, it might be that for the concentrated system ($x = 1$) the bottleneck regime is eventually reached, resulting in a slowing down of the apparent relaxation rate. However, in favor of the presence of an RKKY interaction, we point out that the negative Δg found in this case ($\Delta g = -0.035(5)$, $x = 1$) cannot be due to changes in the local electron density, but should reflect an important distinction between the Fermi surfaces of $\text{LaPt}_4\text{Ge}_{12}$ and $\text{EuPt}_4\text{Ge}_{12}$. Hence, since the presence of d electrons favors the spin-orbit scattering (and thus $1/T_{\text{ceL}}$), the system should not be bottlenecked or, at least, not severely bottlenecked. As an important consequence, the evolution of ΔH is still due to the exchange interaction between the local and itinerant spins, which is now q -dependent.

Figure 7 also reveals a low-temperature increase of ΔH . $\text{EuPt}_4\text{Ge}_{12}$ is known to order magnetically below 1.78 K. Specific heat and dc-susceptibility display four anomalies which indicate a complex magnetic phase diagram [42]. Due to the sensitivity of the ESR technique, it is possible that the broadening of ΔH is related to the magnetic fluctuations which give rise to these different ordered states. The inset shows that the g -value increases for $T \lesssim 20$ K, most likely due to the onset of the internal fields associated with the discussed magnetic phases at low temperatures.

In the whole temperature interval investigated, no indications could be found for an Eu^{2+} rattling behavior. The results of our Q-band investigation are very similar and do not add to our discussion.

C. Possible role of a Raman relaxation

Following the discussion of Dahm *et al.* [26], it is tempting to look for other sources for the relaxation of the localized ions, specially in the case of the Gd-substituted samples. It is possible that the substitution of even a small amount of La by Gd, gives rise to a significant change in the guest vibrational dynamics. In this context it has to be mentioned that a ternary phase $\text{GdPt}_4\text{Ge}_{12}$ does not exist as a stable phase under ambient conditions. Indeed, some threshold requirements have to be fulfilled. Several studies have been devoted to probe high-pressure synthesis routes to compounds that are based on cations with radii below the critical values (see [5] and references therein). However, attempts to synthesize $\text{GdPt}_4\text{Ge}_{12}$ by similar methods failed. Instead, phases with different crystal structures form.

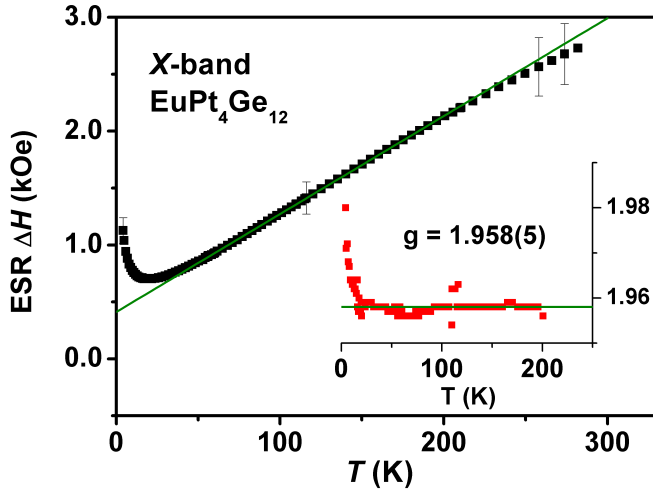


Figure 7: (Color online) X-band ESR linewidth (ΔH) for $\text{EuPt}_4\text{Ge}_{12}$. The thick line is the best fit to the expression $\Delta H(T) = a + bT$, and the obtained coefficients are $a = 412(2)$ Oe and $b = 8.6(1)$ Oe/K. The line describes the behavior of ΔH for $T \geq 50$ K. In the inset, the ESR g -values are presented. For $T \geq 20$ K, $g = 1.958(5)$ is observed, implying in a negative g -shift. Below this temperature the g -values increase (see text for discussion).

The theory of Dahm *et al.* was written in terms of NMR parameters and does not allow to make a direct comparison with our results. Nevertheless, given that the methods for the study of the relaxation processes are quite general, we expect that the qualitative aspects of the theory will remain valid. Therefore, we simply add a scaling parameter to match the theoretical curve with our results.

This theory considers that the guest vibrational dynamics may be described by a Hamiltonian for the anharmonic oscillator, which is treated in a quasi-harmonic approximation. This treatment gives rise to a non-linear equation for an effective frequency which, now, is temperature dependent:

$$\left(\frac{\omega_0}{\omega_{00}}\right)^2 = 1 + \alpha \frac{\omega_{00}}{\omega_0} \left(\frac{1}{\exp(\hbar\omega_0/k_B T) - 1} - \frac{1}{2} + \frac{1}{2} \frac{\omega_0}{\omega_{00}} \right) \quad (5)$$

where ω_0 is the effective phonon frequency, $\alpha > 0$ is a dimensionless parameter characterizing the amount of anharmonicity and $\omega_{00} = \omega_0$ at $T = 0$. In the simplest rattling approximation, $\omega_0 = \omega_{00} = \theta_E$. The relaxation rate $1/T_1 T$ which emerges from this picture gives a fair description of the relaxation phenomena in some skutterudites [19, 23]. It puts forward the idea that the rattling modes have a fundamental role in the spin relaxation of cage systems by inducing an indirect phonon relaxation, usually found in experiments with insulators.

In Fig. 8 we compare our experimental results with the above presented theory. In the NMR experiments [19, 23], the contribution ascribed to the rattling modes

was isolated after a comparison between the relaxation rates of the nuclear spins of the elements in the cage structure, and that of the rattler element. However, since the lattice dynamics of filled skutterudites is determined by significant hybridization of vibrational states of the guest-atoms and of the host structure [6, 7], such a partitioning into independent contributions is not straightforward and therefore should be only a first approximation. Here, even such an approximate “two-site” investigation is not possible. Our choice is to subtract the Korringa rate obtained at Q -band from our linewidth data taken at X -band. We use the results in the case of $\text{La}_{0.9}\text{Gd}_{0.1}\text{Pt}_4\text{Ge}_{12}$, which are obtained in a broader temperature range. In doing that, we assume that the rattling effects in the relaxation are quenched at Q -band and that at X -band one may find both contributions. The value of $\omega_{00} = 24$ K found in this way is considerably lower than $\theta_E = 96$ K obtained from the specific heat of $\text{LaPt}_4\text{Ge}_{12}$ [29]. This result should be interpreted as an extra Einstein mode associated with the Gd^{3+} site, since it is exclusively the Gd^{3+} relaxation which is being probed. It is also expected that, since Gd^{3+} is heavier and significantly smaller than La, it would vibrate with a lower frequency. We also used $\alpha = 5.2$, which is larger than previously reported in the NMR experiments [19, 23], reflecting a stronger anharmonicity due to the inclusion of the Gd^{3+} ions in the oversized cage. We can speculate that the effects of a fully harmonic vibrational dynamics are averaged out and cannot be observed in an ESR experiment, as in the previous section where we addressed the results for the Eu^{2+} ESR. Recent heat capacity measurements, taken at high fields to suppress the superconducting phase, reveal a phonon contribution compatible with an Einstein phonon with $\theta_E \approx 20$ K, in good agreement with our results from ESR [43].

It is important to make an attempt to reconcile the analysis of sections A and C. Dahm *et al* [26] considered that fluctuations in the electron field gradient implied by the rattling behavior provide the mechanism coupling the rattling modes to the relaxation process. In the present case, it is known that the ESR relaxation of a system of spins coupled by an interaction of the RKKY type requires the evaluation of the dynamical part of the RKKY interaction [39]. In this case, a molecular field approximation for the exchange coupling among the spin of the local system should be applied. This molecular field takes into account the finite lattice spacing between the Gd atoms and is determined by the lattice average of the RKKY interaction. Hence, the relaxation of the spin system will be quite sensitive to the lattice parameters. In this direction, we can formulate a scenario where the change of the total vibrational dynamics of the system, as implied by the dynamical behavior (rattling) of the Gd^{3+} ions, generate local fluctuations of the RKKY interaction that are quenched at higher fields. It explains why the evolution of ΔH can be explored with a theory based on a Raman process and is, nevertheless, field dependent. A similar explanation should hold for the ESR

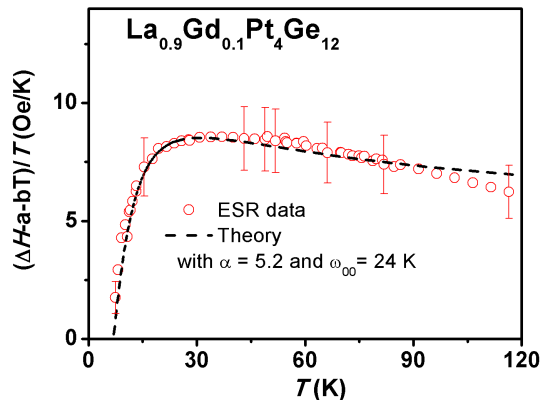


Figure 8: X-band $(\Delta H(T) - a - bT)/T$ for $\text{La}_{0.9}\text{Gd}_{0.1}\text{Pt}_4\text{Ge}_{12}$, where a and b are the parameters determined in the Q -band measurements. The resulting data are compared with the solid line which originates from a theory for spin relaxation due to anharmonic phonons [26]. Parameters that we used (see text) in the calculation are shown in the figure.

on $\text{EuM}_4\text{Sb}_{12}$ ($M=\text{Fe, Ru, Os}$), where the evolution of ΔH was also shown to be field dependent in a similar way.

IV. CONCLUSIONS

In $\text{La}_{1-x}\text{Gd}_x\text{Pt}_4\text{Ge}_{12}$, the relaxation process is non-bottlenecked even for relatively high Gd concentrations. As a consequence, the relaxation process should be determined by the exchange coupling between the local and itinerant spin systems. Besides this result, the effective exchange scattering estimated from the ESR measurements (a microscopic probe), agrees well with the one estimated from the Abrikosov-Gorkov expression for the suppression of T_{sc} (as determined from the total mag-

netization, a macroscopic probe), due to the addition of magnetic ions.

In addition, in X -band it was found that the order of magnitude of the measured g -shifts implies a much smaller relaxation rate than the one observed and it was proposed that the guest vibrational dynamics could give rise to either an enhanced exchange scattering rate or to an additional relaxation process.

The field dependence of the Gd^{3+} ESR relaxation suggests that fluctuations of the RKKY local field, implied by the guest vibrational dynamics, should play a fundamental role in the ESR response of these systems. These were shown to be small fluctuations that are quenched in going from X -band to Q -band measurements, at which one observes a relaxation process as expected in the simplest Korringa picture. An extra phonon mode, to be associated with the vibrational dynamics of the Gd^{3+} ions, was isolated in the $\text{La}_{0.9}\text{Gd}_{0.1}\text{Pt}_4\text{Ge}_{12}$ with $\theta_E \approx 24$ K.

For the Eu-substituted samples, no signatures for rattling behavior were found. The local lattice structure of the Gd^{3+} ions in $\text{LaPt}_4\text{Ge}_{12}$ should be more disordered, due to significant difference in the atoms radii, than that of the Eu^{2+} ions. In this sense, this work provides a microscopic insight on how the local vibrational spectra may change upon small replacements in the guest site.

The evolution of ΔH with T in $\text{La}_{1-x}\text{Eu}_x\text{Pt}_4\text{Ge}_{12}$ is well explained within the simplest approximation of a single-band metal and q -independent J_{eff} for small contents of Eu. The presence of the d electrons at the Fermi surface is suggested by the measured negative g -shift. With increasing content of Eu, larger shifts of the resonance were observed, pointing to a continuous change of the Fermi surface upon Eu substitution. In the case of $\text{EuPt}_4\text{Ge}_{12}$, evidence supporting the Eu^{2+} ions being coupled by the RKKY interaction was found.

In particular, our work adds another piece of evidence for the role of the guest-ion vibrational dynamics in the spin relaxation in metallic compounds, where the Korringa process is expected to dominate.

-
- [1] M. B. Maple, R. E. Baumbach, J. J. Hamlin, D. A. Zocco, B. J. Taylor, N. P. Butch, J. R. Jeffries, S. T. Weir, B. C. Sales, D. Mandrus, et al., *Physica B (Amsterdam, Neth.)* **404**, 2924 (2009).
 - [2] G. J. Snyder and E. S. Toberer, *Nat. Mater.* **7**, 105 (2008).
 - [3] W. Jeitschko and D. Braun, *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry* **33**, 3401 (1977).
 - [4] A. Leithe-Jasper, W. Schnelle, H. Rosner, M. Baenitz, A. Rabis, A. A. Gippius, E. N. Morozova, H. Borrmann, U. Burkhardt, R. Ramlau, et al., *Phys. Rev. B* **70**, 214418 (2004), URL <http://link.aps.org/doi/10.1103/PhysRevB.70.214418>.
 - [5] R. Gumeniuk, H. Borrmann, A. Ormeci, H. Rosner, W. Schnelle, M. Nicklas, Y. Grin, and A. Leithe-Jasper, *Z. Kristallogr.* **225**, 531 (2010), ISSN 0044-2968, URL <http://www.oldenbourg-link.com/doi/abs/10.1524/zkri.2010.1351>.
 - [6] M. M. Koza, L. Capogna, A. Leithe-Jasper, H. Rosner, W. Schnelle, H. Mutka, M. R. Johnson, C. Ritter, and Y. Grin, *Phys. Rev. B* **81**, 174302 (2010), URL <http://link.aps.org/doi/10.1103/PhysRevB.81.174302>.
 - [7] M. M. Koza, A. Leithe-Jasper, H. Rosner, W. Schnelle, H. Mutka, M. R. Johnson, M. Krisch, L. Capogna, and Y. Grin, *Physical Review B* **84**, 014306 (2011), URL <http://link.aps.org/doi/10.1103/PhysRevB.84.014306>.
 - [8] V. Keppens, D. Mandrus, B. C. Sales, B. C. Chakoumakos, P. Dai, R. Coldea, M. B. Maple, D. A. Gajewski, E. J. Freeman, and S. Bennington, *Nature* **395**, 876 (1998), ISSN 0028-0836, URL <http://dx.doi.org/10.1038/395876a0>.

- 1038/27625.
- [9] D. Cao, F. Bridges, P. Chesler, S. Bushart, E. D. Bauer, and M. B. Maple, *Phys. Rev. B* **70**, 094109 (2004), URL <http://link.aps.org/doi/10.1103/PhysRevB.70.094109>.
 - [10] J. Y. Yamaura and Z. Hiroi, *J. Phys. Soc. Jpn.* **80**, 054601 (2011), ISSN 0031-9015, URL <http://jpsj.ipap.jp/link?JPSJ/80/054601/>.
 - [11] M. M. Koza, M. R. Johnson, R. Viennois, H. Mutka, L. Girard, and D. Ravot, *Nat. Mater.* **7**, 805 (2008), ISSN 1476-1122, URL <http://dx.doi.org/10.1038/nmat2260>.
 - [12] W. Schnelle, A. Leithe-Jasper, H. Rosner, R. Cardoso-Gil, R. Gumeniuk, D. Trots, J. A. Mydosh, and Y. Grin, *Phys. Rev. B* **77**, 094421 (2008), URL <http://link.aps.org/doi/10.1103/PhysRevB.77.094421>.
 - [13] T. Goto, Y. Nemoto, K. Sakai, T. Yamaguchi, M. Akatsu, T. Yanagisawa, H. Hazama, K. Onuki, H. Sugawara, and H. Sato, *Phys. Rev. B* **69**, 180511 (2004).
 - [14] M. Tsubota, S. Tsutsui, D. Kikuchi, H. Sugawara, H. Sato, and Y. Murakami, *J. Phys. Soc. Jpn.* **77**, 073601 (2008), ISSN 0031-9015, URL <http://jpsj.ipap.jp/link?JPSJ/77/073601/>.
 - [15] K. Hattori, Y. Hirayama, and K. Miyake, *J. Phys. Soc. Jpn.* **74**, 3306 (2005), ISSN 0031-9015, URL <http://jpsj.ipap.jp/link?JPSJ/74/3306/>.
 - [16] S. Yashiki, S. Kirino, K. Hattori, and K. Ueda, *J. Phys. Soc. Jpn.* **80**, 064701 (2011), ISSN 0031-9015, URL <http://jpsj.ipap.jp/link?JPSJ/80/064701/>.
 - [17] K. Oshiba and T. Hotta, 1105.3811 (2011), URL <http://arxiv.org/abs/1105.3811>.
 - [18] J. Sichelschmidt, W. Carrillo-Cabrera, V. A. Ivanshin, Y. Grin, and F. Steglich, *Eur. Phys. J. B* **46**, 201 (2005), ISSN 1434-6028, URL <http://www.springerlink.com/content/n78gx8728131547t/>.
 - [19] Y. Nakai, K. Ishida, H. Sugawara, D. Kikuchi, and H. Sato, *Phys. Rev. B* **77**, 041101 (2008), URL <http://link.aps.org/doi/10.1103/PhysRevB.77.041101>.
 - [20] L. Holanda, J. Vargas, C. Rettori, P. Pagliuso, E. Bittar, M. Avila, and T. Takabatake, *Physica B (Amsterdam, Neth.)* **404**, 3300 (2009), ISSN 0921-4526, URL <http://www.sciencedirect.com/science/article/pii/S0921452609006176>.
 - [21] B. Nowak, O. Zogal, Z. Henkie, and M. Maple, *Solid State Commun.* **151**, 550 (2011), ISSN 0038-1098, URL <http://www.sciencedirect.com/science/article/pii/S0038109811000408>.
 - [22] F. A. Garcia, C. Adriano, G. G. Cabrera, L. M. Holanda, P. G. Pagliuso, M. A. Avila, S. B. Oseroff, and C. Rettori, 1107.1165 (2011), URL <http://arxiv.org/abs/1107.1165>.
 - [23] F. Kanetake, H. Mukuda, Y. Kitaoka, K.-i. Magishi, H. Sugawara, K. M. Itoh, and E. E. Haller, *J. Phys. Soc. Jpn.* **79**, 063702 (2010), ISSN 0031-9015, URL <http://jpsj.ipap.jp/link?JPSJ/79/063702/>.
 - [24] M. Baenitz, R. Sarkar, R. Gumeniuk, A. Leithe Jasper, W. Schnelle, and M. , *Phys. Status Solidi B* **247**, 740 (2010), ISSN 0370-1972.
 - [25] K. Magishi, H. Sugawara, N. Ohta, T. Saito, and K. Koyama, *Physica C (Amsterdam, Neth.)* **470**, S552 (2010), ISSN 0921-4534, URL <http://www.sciencedirect.com/science/article/pii/S0921453409007953>.
 - [26] T. Dahm and K. Ueda, *Phys. Rev. Lett.* **99**, 187003 (2007), URL <http://link.aps.org/doi/10.1103/PhysRevLett.99.187003>.
 - [27] S. Barnes, *Advances in Physics* **30**, 801 (1981), ISSN 0001-8732.
 - [28] K. Takegahara, H. Harima, and A. Yanase, *J. Phys. Soc. Jpn.* **70**, 1190 (2001).
 - [29] R. Gumeniuk, W. Schnelle, H. Rosner, M. Nicklas, A. Leithe-Jasper, and Y. Grin, *Phys. Rev. Lett.* **100**, 017002 (2008), URL <http://link.aps.org/doi/10.1103/PhysRevLett.100.017002>.
 - [30] A. Maisuradze, W. Schnelle, R. Khasanov, R. Gumeniuk, M. Nicklas, H. Rosner, A. Leithe-Jasper, Y. Grin, A. Amato, and P. Thalmeier, *Phys. Rev. B* **82**, 024524 (2010), URL <http://link.aps.org/doi/10.1103/PhysRevB.82.024524>.
 - [31] M. Toda, H. Sugawara, K.-i. Magishi, T. Saito, K. Koyama, Y. Aoki, and H. Sato, *J. Phys. Soc. Jpn.* **77**, 124702 (2008), ISSN 0031-9015, URL <http://jpsj.ipap.jp/link?JPSJ/77/124702/>.
 - [32] J. P. Joshi and S. V. Bhat, *J. Magn. Reson.* **168**, 284 (2004), ISSN 1090-7807.
 - [33] C. Rettori, D. Davidov, R. Orbach, E. P. Chock, and B. Ricks, *Phys. Rev. B* **7**, 1 (1973), URL <http://link.aps.org/doi/10.1103/PhysRevB.7.1>.
 - [34] C. Rettori, H. M. Kim, E. P. Chock, and D. Davidov, *Phys. Rev. B* **10**, 1826 (1974), URL <http://link.aps.org/doi/10.1103/PhysRevB.10.1826>.
 - [35] D. Davidov, A. Chelkowski, C. Rettori, R. Orbach, and M. B. Maple, *Phys. Rev. B* **7**, 1029 (1973), URL <http://link.aps.org/doi/10.1103/PhysRevB.7.1029>.
 - [36] J. Y. Peng, P. N. Alboni, J. He, B. Zhang, Z. Su, T. Holgate, N. Gothard, and T. M. Tritt, *J. Appl. Phys.* **104**, 053710 (2008), ISSN 00218979, URL <http://link.aip.org/link/JAPIAU/v104/i5/p053710/s1&Agg=doi>.
 - [37] J. Yang, W. Zhang, S. Q. Bai, Z. Mei, and L. D. Chen, *Appl. Phys. Lett.* **90**, 192111 (2007), ISSN 00036951, URL <http://link.aip.org/link/APPLAB/v90/i19/p192111/s1&Agg=doi>.
 - [38] F. A. Garcia, D. J. Garcia, M. A. Avila, J. M. Vargas, P. G. Pagliuso, C. Rettori, M. C. G. Passeggi, S. B. Oseroff, P. Schlottmann, B. Alascio, et al., *Phys. Rev. B* **80**, 052401 (2009), URL <http://link.aps.org/doi/10.1103/PhysRevB.80.052401>.
 - [39] S. E. Barnes, *J. of Phys. F: Metal Phys.* **4**, 1535 (1974), ISSN 0305-4608, URL http://apps.webofknowledge.com/full_record.do?product=UA&search_mode=GeneralSearch&qid=1&SID=4BMPehbnLoo7477o84c&page=2&doc=11.
 - [40] J. R. Schrieffer and P. A. Wolff, *Phys. Rev.* **149**, 491 (1966), URL <http://link.aps.org/doi/10.1103/PhysRev.149.491>.
 - [41] R. H. Taylor and B. R. Coles, *J. of Phys. F: Metal Phys.* **5**, 121 (1975), ISSN 0305-4608, URL <http://iopscience.iop.org/0305-4608/5/1/017>.
 - [42] M. Nicklas, R. Gumeniuk, W. Schnelle, H. Rosner, A. Leithe-Jasper, F. Steglich, and Y. Grin, *Journal of Physics: Conference Series* **273**, 012118 (2011), ISSN 1742-6596, URL <http://iopscience.iop.org/1742-6596/273/1/012118>.
 - [43] W. Schnelle, To be published, (2012).